

Oil Agglomeration of Coal in Salt Solutions:
Effects of Hydrophobicity and Other Parameters on Coal Recovery

C.-W. Fan, R. Markuszewski, and T. D. Wheelock

Ames Laboratory and Department of Chemical Engineering
Iowa State University
Ames, Iowa 50011

Abstract

The recovery of fine coal or graphite particles suspended in water by agglomeration with heptane was observed to be highly dependent on the relative hydrophobicity of the solids as indicated by the measured induction time, i.e., the time required for attachment of one or more particles to a small gas bubble when brought into contact. For highly hydrophobic coal or graphite particles, an increase in ionic strength of the suspending medium caused an increase in agglomeration recovery and a decrease in measured induction time. For weakly hydrophobic coal or pyrite particles, an increase in ionic strength caused a decrease in agglomeration recovery and an increase in induction time. Due to the opposing effects of ionic strength on the recovery of a highly hydrophobic coal and pyrite, it was possible to improve the separation of these materials by an increase in ionic strength. On the other hand, because the recovery of pyrite and a weakly hydrophobic coal were affected similarly by ionic strength, it was not possible to improve the separation of these materials by a similar increase.

Introduction

A number of processes have been proposed for cleaning and recovering ultrafine coal particles suspended in water by selective agglomeration of the carbonaceous solids with oil (1-4). Since most of the ever present mineral impurities are unaffected by oil, an agglomerated suspension can be screened to recover the agglomerates and effect a separation from the unagglomerated mineral particles. The method takes advantage of the difference in surface properties of the organic and inorganic components of coal. Generally the organic material is significantly more hydrophobic than the inorganic minerals found in coal. Therefore, the carbonaceous particles are more readily wetted by oil than the mineral particles, and agglomeration occurs when oil-coated particles become connected by oil bridges. Among the common mineral impurities in coal, only iron pyrite appears to be sufficiently hydrophobic to interfere with separation from coal by this technique. However, the hydrophobicity of pyrite is quite variable and depends on treatment conditions.

It has been recognized that strongly hydrophobic coals respond more readily than weakly hydrophobic coals to this method of treatment (1,5,6). Generally, high recoveries of the more hydrophobic coals can be achieved with relatively small amounts of the lighter, paraffinic hydrocarbons such as heptane, whereas high recoveries of the less hydrophobic coals can only be realized by employing heavier, more complex hydrocarbons in larger amounts. Moreover, for highly hydrophobic coals even less oil is required when the material is suspended in a salt solution (7,8).

An improvement in the separation of coal and pyrite as well as a reduction in oil consumption would improve the economic feasibility of the oil agglomeration method. Minimizing oil consumption by adding salt to the system would reduce one of the major costs of the method. However, preliminary indications suggested that this approach would not work with all types of coal. Therefore, this study was undertaken to determine the effect of coal hydrophobicity on oil agglomeration recovery and to determine how the recovery of different types of coal was affected by salt concentration.

While it was known previously that coal hydrophobicity played an important role in oil agglomeration, it was difficult to measure this role quantitatively. The most popular traditional method for determining wettability by measuring the three-phase contact angle for a water drop on a polished coal surface was difficult to apply in practice. Also it was questionable whether the wettability of a polished surface was the same as that of the small granular particles used in oil agglomeration. In addition, the method was not very sensitive.

Another method of investigating wettability which does not suffer the disadvantages listed above is based on measuring the so-called induction time or, more accurately, the time required for attachment of one or more particles to a small gas bubble when brought into sudden contact under water (9). The measured time is believed to be a combination of the time required to thin the water film between a particle surface and an air bubble to the point of rupture (true induction time) and the time required to displace the film (10,11). Since the attachment time or induction time is based on a dynamic measurement, it depends on the kinetics and hydrodynamics as well as the thermodynamic properties of the system (9-12). Therefore, it differs from the equilibrium contact angle which depends only on the thermodynamic properties of the system. Because of this difference, the induction time depends on certain properties which do not affect the equilibrium contact angle such as particle size and density or the ionic strength of the solution in contact with the particles. Thus, Laskowski and Iskra (12) observed that the induction time of a hydrophobic solid was affected by the concentration of potassium chloride in which the solid was suspended whereas the three-phase contact angle was unaffected. Consequently, certain parameters must be controlled carefully when using induction time measurements to study changes in hydrophobicity.

In the present investigation, the surface of coal and graphite particles was characterized by measuring the induction time, and the response of these materials to agglomeration with heptane was determined by measuring the recovery or mass yield. Different types of coal were utilized which appeared to range from weakly hydrophobic to strongly hydrophobic. In addition, the effect of salt concentration on coal recovery and induction time was determined for a strongly hydrophobic coal (Upper Freeport) and a weakly hydrophobic coal (Illinois No. 6). Also the effect of salt concentration on pyrite recovery and induction time was determined.

Materials and Experimental Methods

Samples of coal were obtained from various sources as indicated in Table 1. The Upper Freeport coal is a medium volatile bituminous coal whereas the other coals are high volatile bituminous coals. Relatively pure samples of graphite from Sri Lanka and mineral pyrite from Huanzala, Peru, were obtained through Ward's Natural Science Establishment. These materials were ground in the dry state with a high-speed impact mill and then screened. For the agglomeration experiments the materials were suspended in deionized water having a resistivity of 17.9 megohm-cm and agglomerated with n-heptane from Eastman Kodak Company. The specified normal boiling point of this material was 98°C which indicated a high level of purity.

The agglomeration experiments were carried out with a specially designed closed system so that the operation was conducted without air present (13). The system utilized the motor and agitator from a 14-speed kitchen blender, but the open container furnished with the blender was replaced by a 500-ml glass jar which was nearly square in cross section. A small hole had been drilled in the bottom of the jar which was plugged with a rubber septum. During operation the jar was inverted, and heptane was introduced through the septum with a hypodermic syringe. For each experiment the jar was completely filled with an aqueous suspension containing either 10 g coal or graphite or 3 g pyrite. In some experiments a suspension containing a mixture of coal and pyrite was employed. The suspension at its natural pH was conditioned for 3 min. at high speed (about 18,000 rpm), and then a predetermined amount of heptane was introduced. Agitation was continued at high speed for 3 min.

Table 1. Sources and properties of coal samples

	Upper Freeport	Pittsburgh	Illinois No. 6	Iowa
Source	Indiana County, PA	Belmont County, Ohio	St. Clair County, IL	Monroe County, IA
Mean diameter ^a , μm	34	39	43	42
Total sulfur, %	2.10	4.03	2.62	3.06
Proximate analysis, %				
Fixed carbon	62.4	48.2	46.5	45.0
Volatile matter	26.8	40.6	34.5	39.1
Ash	10.4	9.8	9.7	12.4
Moisture	0.4	1.4	9.3	3.5
Total	100.0	100.0	100.0	100.0

^aMean diameter of particles used for oil agglomeration.

to produce agglomerates. The agglomerates were recovered on a 100-mesh screen (U.S. Standard), dried in an oven at 100–110°C, and weighed. When a mixture of coal and pyrite was treated, the total sulfur and ash contents of the product were determined and sulfur and ash balances were used to calculate the recovery of the coal and pyrite, respectively.

The so-called induction time of the various materials was measured with the apparatus manufactured by Virginia Coal and Mineral Services, Inc., using the procedure described previously (9–11). For this measurement, -100/+140 mesh coal or graphite particles and -200/+325 mesh pyrite particles were employed. The particles were spread in a thin layer under water and a 2-mm diameter air bubble was formed on the end of a capillary just above the layer of particles. The initial gap between the captive bubble and the surface of the particles was set at approximately 0.1 mm. The bubble was subsequently brought into contact with the particles for successively longer contact times, and the number of particles which adhered to the bubble was noted. The induction time was taken to be the contact time which resulted in particle attachment in five out of ten trials.

Results and Discussion

Graphite and the four coals listed in Table 1 were found to encompass a wide range of hydrophobicity as indicated by the measured induction time. As the results in Table 2 indicate, the induction time ranged from 0.31 ms for graphite (a highly hydrophobic material) to 5.4 ms for Illinois No. 6 coal (a weakly hydrophobic material). For this series of measurements, the particle size was controlled by screening the materials and using only the particles between 100 and 140 mesh. It was necessary to use somewhat larger particles than were used for agglomeration (-200/+400 mesh) to avoid disturbing the bed of particles in the measuring cell when the particles were contacted with a gas bubble. The induction time of the particles used for agglomeration would have been smaller than that of the particles used for determining induction time since the results of Ye et al. (11) indicated that induction time is proportional to particle size raised to a power which depends on particle density. For coal particles of similar density (1.3 to 1.4 g/cm³) the dependency of induction time on particle size was second order, whereas for molybdenite particles (density = 4.7 g/cm³) the dependency was third order. In the

Table 2. Induction time and agglomeration recovery of various carbonaceous materials with heptane

Material	Induction time, ms	Agglomeration recovery, %	
		5 v/v % C ₇ H ₁₆	10 v/v % C ₇ H ₁₆
Graphite	0.31	94	100
Upper Freeport coal	1.96	32	76
Pittsburgh coal	2.25	29	70
Iowa Coal	4.85	6	21
Illinois No. 6 coal	5.40	4	17

present study the induction times of the different coals used for agglomeration should have been approximately 10% of the values listed in Table 2 because of the smaller particle size, and the induction time of graphite even less. The effect of particle size should have been more pronounced for graphite due to its greater density (2.2 g/cm³). Even so, the relative relationship between the induction times of the materials which were agglomerated should have been about as indicated in Table 2.

When the different carbonaceous materials were agglomerated separately with heptane, the recovery decreased monotonically as the induction time of the material increased or, in other words, as the hydrophobicity of the material decreased (see Table 2). This was the case with either 5 or 10 v/v % heptane (i.e., with either 0.5 or 1.0 ml heptane/10 g solids). Thus, there appeared to be a good correlation between recovery and induction time.

The relationship between agglomeration recovery and induction time was explored further by conducting a series of experiments in which different carbonaceous materials were suspended individually in salt solutions and agglomerated with heptane. The results achieved with different salt concentrations are presented in Figures 1 and 2 for Upper Freeport coal and Illinois No. 6 coal, respectively. In the case of the highly hydrophobic Upper Freeport coal, the recovery increased markedly as the salt concentration was raised to 1.5 M, but then it increased only slightly as the salt concentration was raised further to 3.0 M. At this salt concentration, a recovery of 77% was achieved with only 3 v/v % heptane. To obtain a comparable recovery of Illinois No. 6 coal required using 40 v/v % heptane or more. For this weakly hydrophobic coal, the highest recovery was realized when the material was suspended in deionized water, and the recovery decreased when the material was suspended in a salt solution. Moreover the recovery decreased as the salt concentration was increased, and an increase in salt concentration from 0 to 1.5 M produced a greater change in recovery than a further increase from 1.5 to 3.0 M.

The effect of increasing salt concentration on induction time was to reduce the induction time of the highly hydrophobic Upper Freeport coal and increase the induction time of the weakly hydrophobic Illinois No. 6 coal (see Figures 1 and 2). Consequently, the resulting induction time curves were almost mirror images of the recovery curves for the corresponding coals; thus again there seemed to be a close correspondence between recovery and induction time.

The recovery curves and induction time curves for Pittsburgh coal and graphite, while not presented here, were generally similar to those noted above for Upper Freeport coal. Therefore the recovery and induction time of all of these highly hydrophobic materials were affected in the same way by salt concentration. For such materials it appears that the underlying effect of increasing salt concentration or ionic strength of the suspending medium is to compress the electrical double layer surrounding the individual particles (7,8). This in turn destabilizes the water film in contact with the solid according to Laskowski and Iskra (12). Consequently the water film is more easily ruptured between colliding particles and oil droplets or between oil-coated particles. In a similar way the induction time is reduced because the water film between any given particle in contact with a gas bubble also is more easily ruptured.

A different mechanism is required to explain the behavior of Illinois No. 6 coal since an increase in salt concentration produced results which were opposite to those produced in the case of the more hydrophobic coals. One plausible explanation is that the Illinois No. 6 coal adsorbed hydrated sodium ions from the salt solution which made the coal particles more hydrophilic. This would increase the induction time and reduce the agglomeration recovery. Adsorption of sodium ions could likely be due to the presence of oxygen functional groups on the surface of the coal. It is well known that Illinois No. 6 coal has a higher oxygen content than the more hydrophobic coals. Therefore, it would have a greater affinity to adsorb sodium ions.

Pyrite is also known to adsorb sodium ions, with the quantity adsorbed being proportional to the concentration in solution (14). As in the case of Illinois No. 6 coal, this could explain why the pyrite induction time increased and agglomeration recovery decreased when the salt concentration was increased (see Figure 3). Although the curves for pyrite in Figure 3 appeared similar to those for Illinois No. 6 coal in Figure 2, the pyrite was less hydrophobic than the coal. Since pyrite is much denser than coal, smaller particles had to be used for measuring induction time. Because of differences in density and particle size, the induction time of pyrite is therefore not directly comparable with that of the carbonaceous materials. However, the induction time for pyrite was relatively high. Also the agglomeration recovery of pyrite was relatively low, even when 50 v/w % heptane was used.

The opposing influences of salt concentration on the agglomeration recovery of pyrite and Upper Freeport coal suggested a series of experiments in which a mixture of these materials was agglomerated with heptane. The results which were presented in an earlier publication (8) show that coal recovery increased and pyrite recovery decreased as the salt concentration was raised (see Figure 4). Thus the results achieved with the mixture corresponded well with the results of agglomerating the materials separately. Also shown in Figure 4 is the separation efficiency as defined below:

$$\text{Sepn. Eff. (\%)} = \text{Coal Recov. (\%)} - \text{Pyrite Recov. (\%)}$$

It can be seen that the separation efficiency increased with salt concentration until the concentration reached 1.5 M and then remained constant. When a similar set of agglomeration experiments was conducted with a mixture of Illinois No. 6 coal and pyrite, the results were surprising in that the recovery of pyrite was greater than the recovery of coal (see Table 3). On the other hand, when salt was added to the system, the recovery of both materials decreased as expected and the separation suffered.

Conclusions

When aqueous particle suspensions of graphite or various types of coal were agglomerated individually with heptane, the recovery correlated well with the measured induction time which seemed to reflect the natural hydrophobicity of the

Table 3. Results of agglomerating a mixture of Illinois No. 6 coal (5 g) and pyrite (5 g) with heptane

Heptane ml	NaCl M	Final pH	Recovery, %		Separation Eff., %
			Coal	Pyrite	
0.5	0	4.3	15	47	-32
1.0	0	4.3	27	73	-46
2.0	0	4.2	37	87	-50
0.5	1.5	4.1	12	28	-16
1.0	1.5	4.1	19	40	-21
2.0	1.5	4.0	23	43	-20

material. A close correspondence between agglomeration recovery and induction time was also observed in other experiments in which the carbonaceous materials or pyrite were suspended separately in salt solutions of various concentrations. In these experiments, increasing salt concentrations enhanced the recovery and shortened the induction time of highly hydrophobic solids but reduced the recovery and lengthened the induction time of weakly hydrophobic solids. The effect of salt concentration on the highly hydrophobic solids appeared to be due to compression of the electrical double layer surrounding individual particles, whereas the effect on weakly hydrophobic particles seemed to be due to adsorption of hydrated cations. Because of these differing effects, it was possible to improve the separation of highly hydrophobic Upper Freeport coal and pyrite by increasing the salt concentration of the agglomeration system, but it was not possible to improve the separation of weakly hydrophobic Illinois No. 6 coal and pyrite.

Acknowledgement

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This work was supported by the Assistant Secretary for Fossil Energy, through the Pittsburgh Energy Technology Center.

Literature Cited

1. C. E. Capes and J. R. Germain, "Selective Oil Agglomeration in Fine Coal Beneficiation," Chapter 6 in: Physical Cleaning of Coal, Y. A. Liu (ed.), Marcel Dekker, New York, 1982.
2. V. P. Mehrotra, K. V. S. Sastry and B. W. Morey, "Review of Oil Agglomeration Techniques for Processing of Fine Coals," International Journal of Mineral Processing, 11, 175-201 (1983).
3. T. D. Wheelock and R. Markuszewski, "Coal Preparation and Cleaning," Chapter 3 in: The Science and Technology of Coal and Coal Utilization, B. R. Cooper and W. A. Ellingson (eds.), Plenum Press, New York, 1984.
4. W. G. Steedman and S. V. Krishnan, "Oil Agglomeration Process for the Treatment of Fine Coal," Chapter 8 in: Fine Coal Processing, S. K. Mishra and R. R. Klimpel (eds.), Noyes Publications, Park Ridge, New Jersey, 1987.
5. R. Venkatadri, R. Markuszewski, and T. D. Wheelock, "Oil Agglomeration of Weakly Hydrophobic Coals and Coal/Pyrite Mixtures," Energy & Fuels, 2 (2), 145-150 (1988).

6. Z. Sadowski, R. Venkatadri, J. M. Druding, R. Markuszewski, and T. D. Wheelock, "Behavior of Oxidized Coal during Oil Agglomeration," Coal Preparation (in press).
7. G. C. C. Yang, R. Markuszewski and T. D. Wheelock, "Oil Agglomeration of Coal in Inorganic Salt Solutions," Coal Preparation, 5 (3-4), 133-146 (1988).
8. C.-W. Fan, R. Markuszewski, and T. D. Wheelock, "Coal and Pyrite Separation by Oil Agglomeration in Salt Solutions," Fizykochemiczne Problemy Mineralurgii, 19, 17-26 (1987).
9. J. L. Yordan and R. H. Yoon, "Induction Time Measurements for the Quartz-Amine Flotation System," Preprint No. 86-105 for Society of Mining Engineering Annual Meeting, New Orleans, March 2-6, 1986.
10. Y. Ye and J. D. Miller, "Bubble/Particle Contact Time in the Analysis of Coal Flotation," Coal Preparation, 5, 147-166 (1988).
11. Y. Ye, S. M. Khandrika and J. D. Miller, "Induction-Time Measurements at a Particle Bed," presented at 117th AIME Annual Meeting, Phoenix, Arizona, Jan. 25-28, 1988.
12. J. Laskowski and J. Iskra, "Role of Capillary Effects in Bubble-Particle Collision in Flotation," Transactions Institution Mining and Metallurgy, Sec. C Mineral Processing and Extractive Metallurgy, 79, C6-C10 (1970).
13. J. Drzymala, R. Markuszewski and T. D. Wheelock, "Influence of Air on Oil Agglomeration of Carbonaceous Solids in Aqueous Suspension," International Journal of Mineral Processing, 18, 227-286 (1986).
14. A. M. Gaudin and W. D. Charles, "Adsorption of Calcium and Sodium on Pyrite," Transactions of AIME, 196, 195-200 (1953).

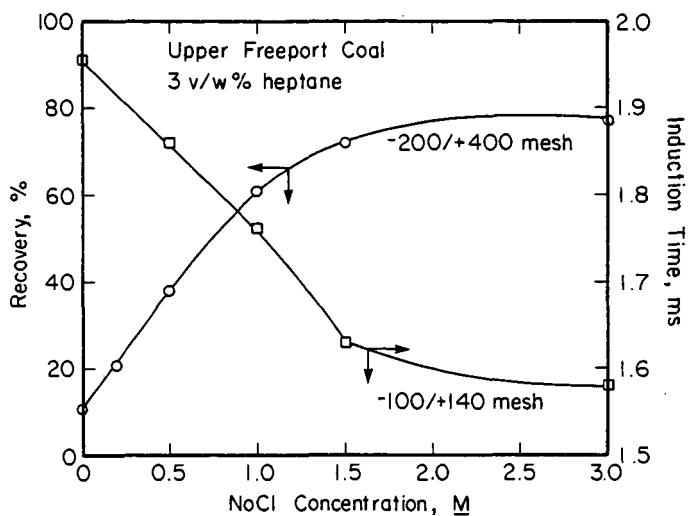


Figure 1. Effect of salt concentration on Upper Freeport coal recovery and induction time.

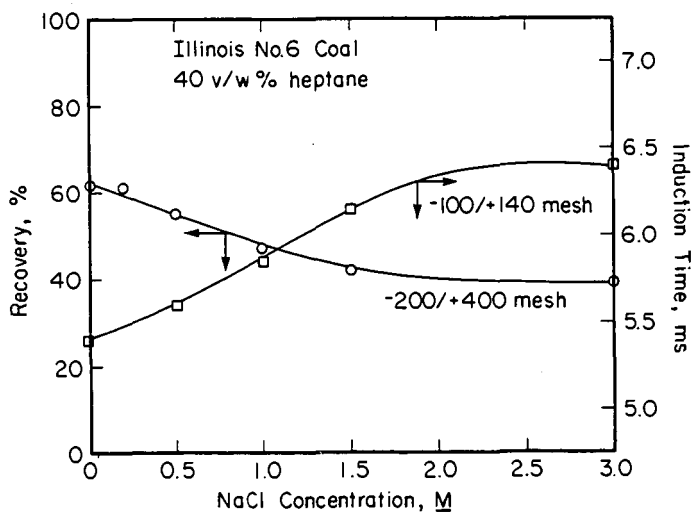


Figure 2. Effect of salt concentration on Illinois No. 6 coal recovery and induction time.

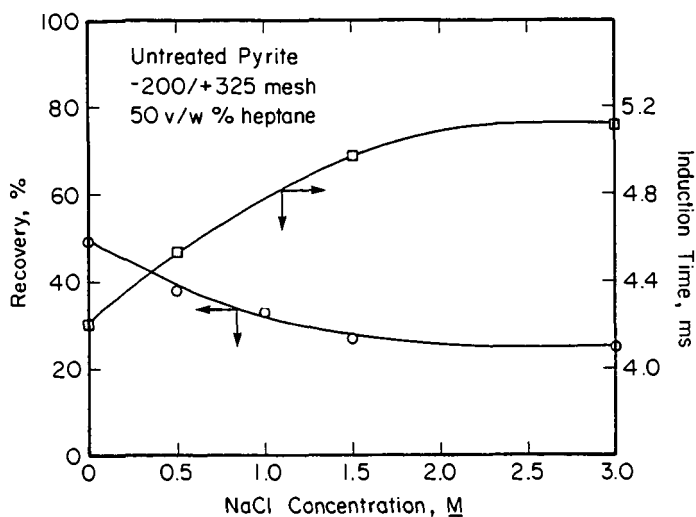


Figure 3. Effect of salt concentration on mineral pyrite recovery and induction time.

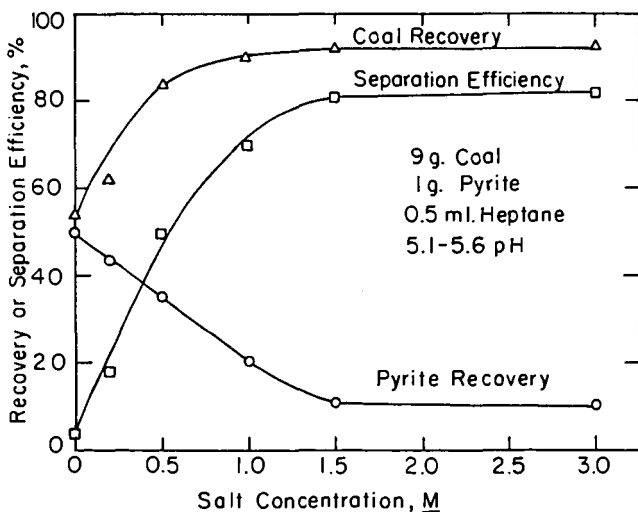


Figure 4. Results of agglomerating a mixture of Upper Freeport coal and pyrite (Ref. 8).